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INFRARED PHOTOLUMINESCENCE SPECTRA OF PBS NANOPARTICLES PREPARED BY THE LANGMUIR-BLODGETT AND LASER ABLATION METHODS

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Abstract. We have optimized the optical setup originally designed for photoluminescence measurements in the spectral range 400–1100 nm. The new design extends the spectral range into the near infrared region 900–1700 nm and enables colloidal solution measurements in cuvettes as well as measurements of nanoparticles deposited in the form of thin films on glass substrates. The infrared photoluminescence spectra of PbS nanoparticles prepared by the Langmuir-Blodgett technique show higher photoluminescence intensity and a shift to shorter wavelengths than the infrared photoluminescence spectra of PbS nanoparticles prepared by laser ablation from a PbS target. We also have proved that PbS nanoparticles prepared in the form of thin layers have high stability.

Keywords: Infrared photoluminescence, PbS, Langmuir–Blodgett, laser ablation.

1. Introduction

In the visible spectral region, functionally specific targeting and imaging have been demonstrated using semiconductor nanoparticles [1]. Using visible fluorescent tags, however, deep organs such as the liver and the spleen could not be detected because of the limited penetration depth of visible light. Deep-tissue imaging requires the use of infrared light within a spectral window separated from the major absorption peaks of hemoglobin and water. Infrared optical imaging of living tissue is therefore an area of growing interest, for example to provide improved tumor-sensitivity. High-transparency spectral bands in the near infrared region enable depths of detection of 5–10 cm, a capability that provides surgeons with direct infrared visual guidance throughout a sentinel-lymph-node mapping procedure, minimizing incision and dissection inaccuracies and permitting real-time confirmation of complete resection [2].

Infrared light-emitting diodes based on nanoparticles have the potential to offer low manufacturing cost, compatibility with a range of substrates and quantum-size-effect tunability. They can be integrated on CMOS-processed silicon electronics in chip-to-chip and board-to-board optical interconnections and in fiber-optic and optical wireless communications. Large-area infrared emitters for biomedical imaging would enable optical diagnosis in near infrared biological transparency windows [3].

Photoluminescence (PL) spectroscopy is a powerful technique for investigating semiconducting and semi-insulating nanoparticles [4]. We apply infrared PL to study the relative PL quantum efficiency and the thermal stability of PbS nanoparticles prepared in the form of thin layers by the Langmuir–Blodgett and laser ablation methods on glass substrates.

2. Experimental part

Samples of thin-layered amorphous hydrogenated silicon with embedded lead sulphide (PbS) nanoparticles were prepared in the combined radio frequency (13.56 MHz) plasma-enhanced chemical vapor deposition (CVD) and reactive laser ablation reactor. The reactor was designed by ing. J. Stuchlik, from the Institute of Physics of the Academy of Sciences of the Czech Republic (ASCR), v.v.i., Prague, and it is being developed at the Institute of Chemical Process Fundamentals of the ASCR, v.v.i. in Prague for *in-situ* growth, deposition and embedding of nanoparticles in a-Si:H based PIN and LED structures. The 2-litre glass capacitively coupled plasma (CCP) reactor is equipped with:

- two electrodes for deposition of silicon layers (glass and copper substrates were fixed to the grounded substrate);
- a quartz window entrance for a focused laser beam;
- a PbS target for ablation.

The reactor can be evacuated down to 10^{-3} Pa. The PbS nanoparticles are deposited by ablation of a solid PbS target (diameter 9 mm) in a vacuum (ArF ex-

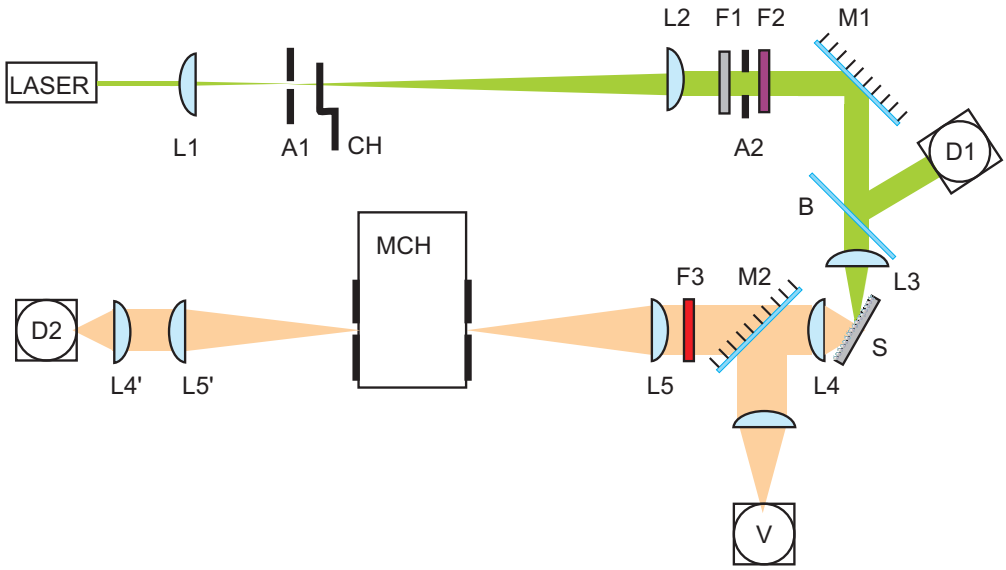

FIGURE 1. Photoluminescence setup: LASER: excitation light source, L1–5: fused silica lens 1" in diameter, Ch: chopper, A1–2: apertures, F1–4: optical filters (F1: grey filters, F2: band pass filters, F3: long-pass filter), D1–2: detectors connected to lock-in amplifiers referenced to the chopper frequency, M1–2: mirrors (M2 is removable), B: beamsplitter, MCH: Horiba H20IR monochromator, S: sample.

cimer laser operating at 193 nm, energy 60 mJ/pulse, 600 pulses). For the purposes of this study, PbS deposition was conducted at room temperature on Corning glass #7059 substrates using only laser ablation without CCP plasma. The thickness measured by an Alpha step 100 profilometer was about 50 nm.

High quality samples with PbS nanocrystals on a fused silica substrate were prepared using the Langmuir-Blodgett (LB) technique at the Institute of Semiconductor Physics in Novosibirsk, Russia. For this purpose, LB films of lead behenate were grown by substrate transfer through monolayers (ML) formed on the liquid subphase surface, comprising lead nitrate. Monolayer transfer was carried out by Y-type at a surface pressure of 30 mN/m and a temperature of 22 °C. Using this method, samples containing up to hundreds of monolayers can be prepared with a typical nanoparticle diameter of 3–10 nm (K. Zhuravlev, private communication). Sulphurizing the films using hydrogen sulfide gas was carried out for a period of 1–1.5 hours at a pressure of 7–13 kPa and a temperature of 22 °C. As a result of the interaction between lead behenate and hydrogen sulfide, PbS NCs distributed in the LB matrix were formed. The final step was to remove the LB film matrix by thermally-induced desorption of the behenic acid in ammonia and argon gas under atmospheric pressure at temperatures of 100 and 200 °C.

The steady-state photoluminescence spectra were measured at the Institute of Physics of the ASCR, v.v.i. in Prague by the setup depicted in Fig. 1. The essential components in this setup are a green laser, which is used as the excitation energy source, the objective *L5* collecting the photoluminescence signal with a relative aperture of $f/1$, the monochromator (*MCH2*) and the InGaAs photodiode (*D2*) to detect the photoluminescence spectra.

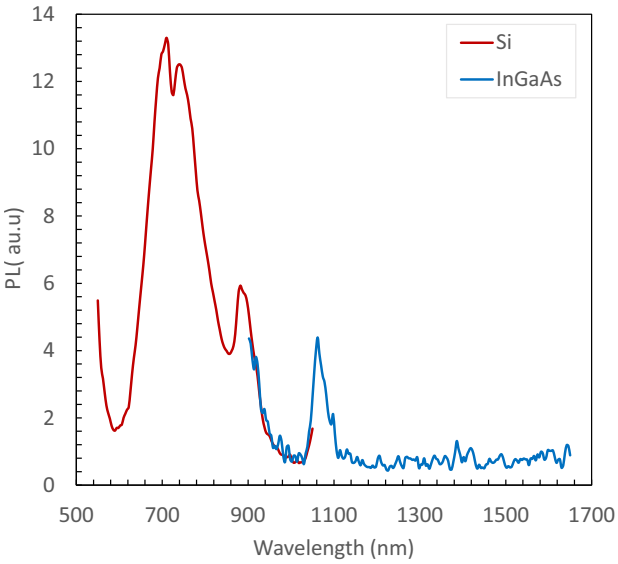

FIGURE 2. The spectrally corrected and normalised photoluminescence spectrum of the Corning glass #7059 substrate measured by Si (550–1050 nm) and InGaAs (900–1650 nm) photodiodes.

3. Results and Discussion

Unlike fused silica glass, other types of glass show significant photoluminescence. The spectrally corrected and normalized photoluminescence spectrum of a clean Corning glass #7059 substrate is shown in Fig. 2. The higher noise in the IR spectra is due to the lower detectivity of the InGaAs photodiode. The IR spectrum is dominated by the glass-related PL band at wavelengths 850–950 nm and the PL band centered at 1064 nm. However, no measurable photoluminescence was detected on fused silica glass.

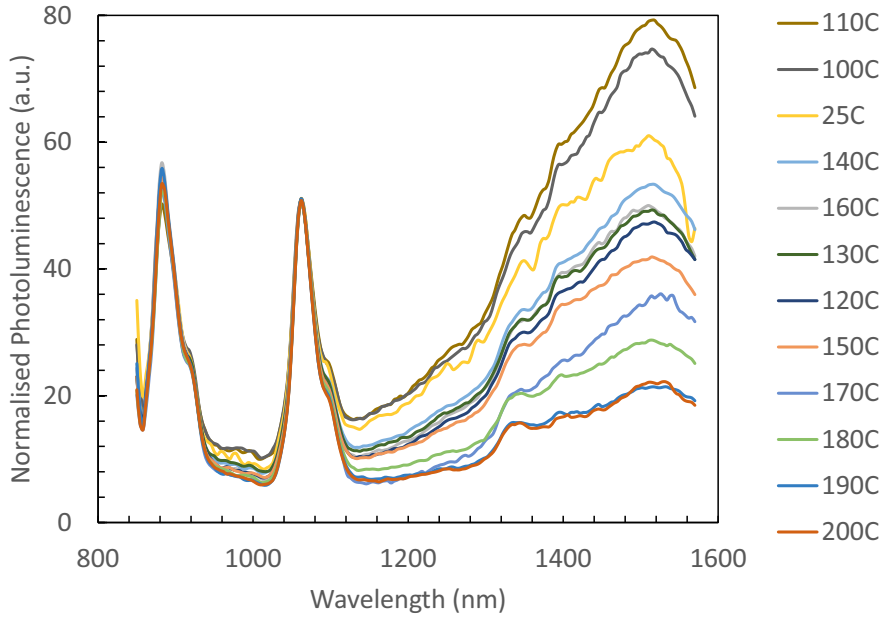

Figure 3. The room temperature spectrally corrected and normalized PL spectra of a 50 nm layer of PbS nanoparticles deposited on a Corning glass #7059 substrate and annealed for 5 min in air at various temperatures. The spectra were normalised on the peak intensity at 1064 nm.

The normalized spectra in Fig. 3 clearly show the trends of PbS nanoparticle-related PL upon annealing in air at various temperatures. The glass related PL bands at 850–950 nm and at 1064 nm are assumed to be constant. Therefore, the variations in their intensity in the spectrally corrected spectra are random changes related to handling the sample. We therefore normalized the corrected spectra on the peak intensity at 1064 nm, see Fig. 3. First of all, the PL spectra show the maximum at 1530 nm and prove that PbS nanoparticles are stable at room temperatures with no observable changes in the as-grown samples in a period of several months between the first measurements and the late measurements. We have observed that PL can be enhanced by moderate annealing at temperatures of about 110 °C. We speculate that this PL enhancement may be due to drying nanoparticles, but this hypothesis must be confirmed by further studies. However, after annealing at higher temperatures the PL intensity gradually deteriorates with increasing temperature.

In Fig. 4, we compare a thin layer of PbS nanoparticles prepared by the Langmuir-Blodgett technique and laser ablation from the PbS target with both samples annealed at 110 °C to promote infrared photoluminescence. The comparison clearly shows higher intensity of the infrared photoluminescence of the PbS nanoparticles prepared by the Langmuir-Blodgett technique, and also a shift of the maximum photoluminescence to shorter wavelengths. This indicates the smaller size of the PbS nanoparticles deposited by the Langmuir-Blodgett technique. It should be noted that the Langmuir-Blodgett technique is a well optimized process at the Institute of Semiconductor Physics in Novosibirsk, Russia, whereas PbS deposition by the laser ablation technique at the Institute of Chemical Process Fundamentals of the ASCR, v.v.i. in Prague has only recently been started. More optimization is therefore needed to enhance the quantum efficiency of PbS nanoparticles deposited by the laser ablation technique. One way to achieve PbS nanoparticles of smaller size and with higher quantum efficiency is to apply reactive laser ablation of the metallic Pb target in an H_2S atmosphere [5].

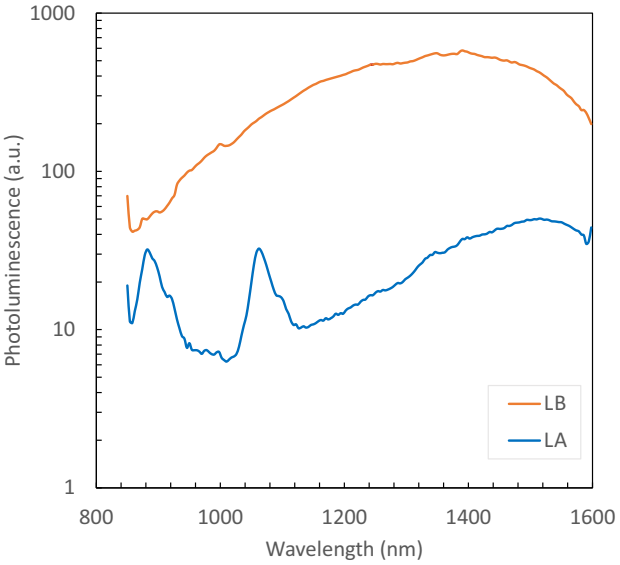

Figure 4. A room temperature comparison of the logarithmic scale intensity of the photoluminescence spectra of a layer of PbS nanoparticles about 50 nm in thickness prepared by the laser ablation method (LA, on Corning glass 7059) and by the Langmuir-Blodgett method (LB, on fused silica glass).

4. Conclusion

We have investigated the thermal stability of PbS nanoparticles deposited as a thin film on glass substrates by laser ablation from a PbS target. We have discussed in detail the calibration procedures used to correct the spectra on the spectral efficiency of the setup. We have shown the importance of the background signal for normalizing the PL spectra and have proved that the PbS nanoparticles have high stability. The infrared photoluminescence spectra of the PbS nanoparticles prepared by the Langmuir-Blodgett technique clearly show higher photoluminescence intensity and a shift to shorter wavelengths than the infrared photoluminescence spectra of PbS nanoparticles prepared by laser ablation from the PbS target. More optimization is therefore needed to reduce the size of the PbS nanoparticles deposited by the laser ablation technique.

Acknowledgements

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